APPLICATION OF PHOTON STATISTICS TO THE SPECIFIC HEAT OF A MONATOMIC SOLID

By B. N. BISWAS

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ABSTRACT. In the present paper, the statistics of photons, as developed by the author in a previous paper, has been applied to derive an expression for the specific heat of a monatomic solid, the molecules of which are endowed with three degrees of freedom. The expression thus found is similar to Debye's expression for the specific heat of a monatomic solid. Expressions for the entropy and free energy of the solid have also been worked out.

SUMMARY OF STATISTICS OF PHOTONS

Black radiation contained in a chamber at any temperature is assumed to consist of photons in thermal equilibrium. The whole of the phase space representing them is divided into cells of volume h^3.

Number of cells contained in the energy layers $h\nu$ and $h(\nu+d\nu)$ in the phase space

$$V \times 4\pi\nu^2 \times d\nu \qquad \ldots \quad (1)$$

where V is the volume of the black chamber.

The total number of cells to be considered in the phase space within the energy layers $h\nu$ and $h(\nu+d\nu)$

$$= \frac{8\pi V.\nu^2.d\nu}{c^3} \qquad \ldots \quad (2)$$

in view of polarisation.

In this domain of the phase space, some cells will remain empty, some will contain one representative point, some two, and so on.

C_r = number of cells containing r representative points ($r = 0, 1, 2, \ldots$)

$$= \frac{8\pi V.\nu^2}{c^3}\left(1 - e^{-\frac{h\nu}{kT}}\right)e^{-r\frac{h\nu}{kT}}. \qquad \ldots \quad (3)$$

The total number of photons represented in the same phase space,

$N = C_1 + 2C_2 + 3C_3 + \ldots$

$$= \frac{8\pi V.\nu^2.d\nu}{c^3}\left(1 - e^{-\frac{h\nu}{kT}}\right)\left[e^{-\frac{h\nu}{kT}} + 2.e^{-2\frac{h\nu}{kT}} + 3.e^{-3\frac{h\nu}{kT}} + \ldots\right]$$

$$= \frac{8\pi V.\nu^2.d\nu}{c^3} \times \frac{1}{e^{h\nu/kT} - 1}. \qquad \ldots \quad (4)$$

Total amount of energy associated with photons of frequency

$$E=\frac{8\pi V.\nu^2.d\nu}{c^3}\times\frac{h\nu}{e^{h\nu/kT}-1}. \qquad \ldots (5)$$

Entropy of the same photons,

$$S=\frac{8\pi k.V.\nu^2 d\nu}{c^2}\left\{\frac{\frac{h\nu}{kT}}{e^{h\nu/kT}-1}-\log\left(1-e^{-\frac{h\nu}{kT}}\right)\right\}. \qquad \ldots (6)$$

Free energy of the same photons,

$$F=\frac{8\pi V.k.T.\nu^2}{c^3}\log\left(1-e^{-\frac{h\nu}{kT}}\right). \qquad \ldots (7)$$

STATISTICAL THEORY OF SPECIFIC HEAT OF A MONATOMIC SOLID

The molecular weight of a monatomic solid contains N atoms, N being Avogadro's number. Hence the system has 3N degrees of freedom. The degree of freedom is defined here by the number of independent terms contained in the expression for its energy. Thus the expression for the heat content of a monatomic solid would consist of 3N terms. In order to derive the law of partition of energy in this case, from the principles of statistics of photons, quantised waves in ether having been replaced by photons, the solid, as a whole, is assumed to be a continuous elastic medium in which energy is associated with two types of waves, longitudinal and transverse. Each of these two types of waves is assumed to be quantised. Hence it can be replaced by photons. Longitudinal waves of frequency ν are replaced by photons, called afterwards as longitudinal photons of frequency ν, each of energy $h\nu$ and momentum $h\nu/C_L$ where C_L is the velocity of the longitudinal wave in the elastic solid and is equal to $\sqrt{K+\frac{4n}{3}/\rho}$. Similarly, transverse waves, by photons of frequency ν, called transverse photons, each of energy $h\nu$ and momentum $h\nu/C_T$ where C_T is the velocity of the transverse waves in the solid and is equal to $\sqrt{n/\rho}$; K is the bulk modulus of elasticity and n the coefficient of rigidity and ρ the density of the medium.

The expression for the energy of the solid would, in the light of the assumptions made above, include as many independent terms as the number of cells required in the phase space to represent all the photons in the phase space, the energy of a cell being equal to the energy of photons, the representative points of which are enclosed by the cell. Hence their total number must be 3N.

Thus, 3N = number of cells for longitudinal photons

+ number of cells for transverse photons

$$=4\pi V\int_0^{\nu}\left(\frac{1}{C_T^3}+\frac{2}{C_L^3}\right)d\nu. \qquad (8)$$

From (1) and (2), the upper limit must be a definite quantity as the L.H.S.E. is definite. The upper limit obviously depends on the nature of the substance in view of 3N being independent of the nature of the substance, V, of course, stands for the volume of the solid.

or,
$$3\mathrm{N} = \frac{4\pi \mathrm{V} \nu_m^3}{3}\left[\frac{1}{\mathrm{C}_{\mathrm{L}}^3} + \frac{2}{\mathrm{C}_{\mathrm{T}}^3}\right]$$

$$\nu_m^3 = \frac{9\mathrm{N}}{4\pi\mathrm{V}\left[\frac{1}{\mathrm{C}_{\mathrm{L}}^3} + \frac{2}{\mathrm{C}_{\mathrm{T}}^3}\right]}, \qquad \ldots \quad (9)$$

Energy associated with both types of photons of frequency ν is, according to (5),

$$= 4\pi\mathrm{V}\left[\frac{1}{\mathrm{C}_{\mathrm{L}}^3} + \frac{2}{\mathrm{C}_{\mathrm{T}}^3}\right] \times \frac{h\nu^3}{e^{h\nu/k\mathrm{T}} - 1}\, d\nu. \qquad \ldots \quad (10)$$

Heat content of the solid

$$= 4\pi\mathrm{V}\left[\frac{1}{\mathrm{C}_{\mathrm{L}}^3} + \frac{2}{\mathrm{C}_{\mathrm{T}}^3}\right] \int_0^{\nu_m} \frac{h\nu^3}{e^{\frac{h\nu}{k\mathrm{T}}} - 1}\, d\nu$$

$$= \frac{9\mathrm{N}}{\nu_m^3} \int_0^{\nu_m} \frac{h\nu^3}{e^{\frac{h\nu}{k\mathrm{T}}} - 1}. \qquad \ldots \quad (11)$$

On putting $\frac{h\nu}{k\mathrm{T}} = \epsilon$, $\frac{h\nu_m}{k} = \theta$ and $\frac{\theta}{\mathrm{T}} = \epsilon_m$, we have

$$\mathrm{U} = 9\mathrm{R}\mathrm{T}\left(\frac{\mathrm{T}}{\theta}\right)^3 \int_0^{\epsilon_m} \frac{\epsilon^3 . d\epsilon}{e^{\epsilon} - 1} \qquad \ldots \quad (11a)$$

$$\mathrm{C}_v = \frac{d\mathrm{U}}{d\mathrm{T}} = 9\mathrm{R}\frac{\mathrm{T}^3}{\theta^3} \times \int_0^{\mathrm{T}} \frac{e^{\epsilon}}{(e^{\epsilon} - 1)^2}\, d\epsilon$$

$$= 3\mathrm{R}\left[\frac{12}{x^3}\int_0^{x} \frac{\epsilon^3}{e^{\epsilon} - 1}\, d\epsilon - \frac{3x}{e^{x} - 1}\right], \qquad \ldots \quad (11b)$$

putting
$$x = \epsilon_m = \frac{\theta}{\mathrm{T}},$$

which is the same as Debye's expression for the specific heat of a monatomic solid.

From (6) and (9) we have entropy of the solid,

$$\mathrm{S} = \frac{9\mathrm{N}k}{\nu_m^3}\left[\int_0^{\nu_m}\left\{\frac{\frac{h\nu^3}{k\mathrm{T}}}{e^{\frac{h\nu}{k\mathrm{T}}} - 1} - \nu^2 \log\left(1 - e^{-\frac{h\nu}{k\mathrm{T}}}\right)\right\}.d\nu\right] \qquad \ldots \quad (12)$$

excluding the constant term,

$$= \frac{9NkT}{\theta^3}\int_0^{\epsilon_m}\frac{\epsilon^3.d\epsilon}{e^{\epsilon}-1} - \frac{9NkT^3}{\theta^3}\int_0^{\epsilon_m}\epsilon^2.\log\left(1-e^{-\epsilon}\right).d\epsilon \qquad \ldots \quad (12a)$$

on making the same substitutions as before.

$$S = \frac{12NkT^3}{\theta^3}\int_0^{\frac{\theta}{T}}\frac{\epsilon^3}{e^{\epsilon}-1}.d\epsilon - 3Nk\log\left(1-e^{-\frac{\theta}{T}}\right) \qquad \ldots \quad (12b)^*$$

which is the general expression for the entropy of the solid, excluding the constant term.

APPROXIMATIONS AT LOW AND HIGH TEMPERATURES

(*i*) *Low temperature*—

At very low temperatures, $T<<\theta$, consequently equation (12*a*) assumes the following form :

$$S = \frac{9N.kT^3}{\theta^3}\int_0^{\infty}\frac{\epsilon^3}{e^{\epsilon}-1}d\epsilon - \frac{9N.kT^3}{\theta^3}\int_0^{\infty}\epsilon^2.\log\left(1-e^{-\epsilon}\right).d\epsilon$$

$$= \frac{4\pi^4}{5}\times\frac{N.k.T^3}{\theta^3} \qquad \ldots \quad (12c)\dagger$$

excluding the constant terms.

(*ii*) *High temperature*—

$$T>>\theta$$

Equation (12*a*) assumes the following form :

$$S = \frac{9NkT^3}{\theta^3}\int_0^{\epsilon_m}\frac{\epsilon^3.d\epsilon}{e^{\epsilon}-1} - \frac{9NkT^3}{\theta^3}\int_0^{\epsilon_m}\epsilon^2.\log\left(1-e^{-\epsilon}\right).d\epsilon$$

$$= 4Nk + 3Nk\log\frac{T}{\theta} \qquad \ldots \quad (12d)\ddagger$$

excluding the constant term.

From (7) and (9) we have free energy of the solid

$$F = \frac{9N.kT}{\nu_m^3}\int_0^{\nu_m}\nu^2.\log\left(1-e^{-\frac{h\nu}{kT}}\right)d\nu, \text{ excluding the constant term.}$$

$$= 9kT\left(\frac{T}{\theta}\right)^3\int_0^{\epsilon_m}\epsilon^2.\log\left(1-e^{-\epsilon}\right)d\epsilon \qquad \ldots \quad (13)$$

$$= 3NkT\log\left(1-e^{-\frac{\theta}{T}}\right) - \frac{3NkT^4}{\theta^3}\int_0^{\frac{\theta}{T}}\frac{\epsilon^3}{e^{\epsilon}-1}.d\epsilon \qquad \ldots \quad (14)$$

which is the general expression for the free energy, excluding the constant term.

* *Vide* p. 591, *The Principles of Statistical Mechanics*, *Tolman*, equation (137.36).

† *Vide* p. 591, *Tolman*, equation (137.37).

‡ *Vide* p. 590, *Tolman*, equation (137.34).

(*i*) *Low temperature, i.e.,* $T << \theta$

The equation (13) assumes the following form :

$$F = 9NkT\left(\frac{T}{\theta}\right)^3 \int_0^{\infty} \epsilon^2 . \log\,(1 - e^{-\epsilon}).d\epsilon$$

$$= -\frac{NkT^4\pi^4}{5\theta^3} \tag{15}$$

excluding the constant term.

(*ii*) *High temperature, i.e.,* $T >> \theta$.

From (13) we have

$$F = 9NkT\left(\frac{T}{\theta}\right)^3 \int^{\frac{\theta}{T}} \epsilon^2 . \log\,\epsilon.d\epsilon$$

$$= 3NkT\;\log\frac{\theta}{T} - NkT, \tag{16}$$

excluding the constant term.

PHYSICAL LABORATORY,
RAJARAM COLLEGE,
KOLHAPUR.

REFERENCE

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